

# PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

### Catalytic Halogenation of Hydrocarbons

We, PULLMAN INCORPORATED, a corporation organised under the laws of the State of Delaware, United States of America, of 200 South Michigan Avenue, Chicago, State of Illinois, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for polyhalogenating an unsubstituted or halogen substituted hydrocarbon containing at least one hydrogen atom of the olefinic or aromatically unsaturated type.

The halogenation of hydrocarbons with oxygen or air and a hydrogen halide in the presence of a metal halide catalyst is a process of primary importance in the commercial production of halogenated hydrocarbons of both saturated and unsaturated types. The catalysts heretofore employed in these halogenation processes are most usually halides of metals having variable valences or oxy halides of these metals. As employed in these reactions, the catalysts are usually deposited on solid carriers such as pumice, various natural clays, kieselguhr, alumina or silica or any other attrition-resistant carrier material and the solid mass is employed in the chlorination of hydrocarbons, either in a fixed or moving bed or in a fluidized state in a reaction zone.

The commercial success of these processes is due largely to the demand for halogenated compounds containing from 1 to 6 carbon atoms; however, there is a great need for improvement in these processes. For example, it would be highly desirable to reduce the contact time normally associated with fixed bed operation, while eliminating the difficulties associated with fluidized

solid operation such as catalyst attrition and catalyst vaporization which appears to be more pronounced with highly active catalysts. While the moving bed solves some of these difficulties, it is not without its own particular problems such as those derived from the mechanical transportation of catalyst throughout a zone and the existence of "hot spots" in the catalyst bed. The heat of reaction generated on the surface of the solid permits direct oxidation of the hydrocarbon to produce undesirable oxides of carbon.

The more active metal halide catalysts, such as, for example, copper chloride are more volatile at required halogenation temperatures and thus, it is difficult to retain the catalyst in the system and maintain the activity of the catalyst mass over an extended period of time. In such systems the volatilized catalyst must be recovered by condensation or other troublesome methods and returned in a supported state to the reaction zone. Thus, the economics of operating with fluidized catalyst is poor in spite of the fact that such a system provides better temperature control and higher yield of product for a given period of operation.

It is also desired that the metal halide catalyst composition be readily regenerated and reused in the chlorination process.

In accordance with the present invention there is provided a process for polyhalogenating an unsubstituted or halogen-substituted hydrocarbon containing at least one hydrogen atom of the olefinic or aromatically unsaturated type which comprises reacting the hydrocarbon with an aqueous composition comprising an aqueous solution of cupric halide or ferric halide and as a promoter at least one halide of a dissimilar element, or a dissimilar valence state of the same

[Price

element, said element being copper, silver, gold, zinc, cadmium, mercury, boron, aluminum, gallium, indium, thallium, titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, manganese, tungsten, iron, tin, bismuth, cobalt, or nickel, the concentration of the total halides in aqueous solution being between 0.001 mol per cent and 50 mol per cent, preferably between 10 mol per cent and 30 mol per cent.

The catalyst composition may contain some of the halide in suspension as well as in solution.

Halogenation reactions with such halide catalysts can be carried out at lower temperatures than heretofore employed, for example, halogenation of an olefin can be carried out at a temperature between 120° C. and 180° C. under pressure sufficient to maintain the catalyst liquid phase. Broadly, for the purposes of the present invention, the halogenation temperature employed may be as high as 350° C., particularly in cases where aromatically unsaturated compounds are reacted. However, it is to be understood that still higher temperatures can be employed if desired, even though the conversion to halogenated hydrocarbon is not measurably improved. It is found that at higher temperatures carbon dioxide is formed in the reaction which lowers the selectivity of the present process in the formation of halogenated product, and is particularly detrimental to the selectivity of 1,2 - dichloroethane when ethylene is the hydrocarbon. Thus, the CO<sub>2</sub> formation should be maintained below 5 per cent of the hydrocarbon feed. The pressures employed in the halogenation reactions can vary from atmospheric pressure up to 1,000 p.s.i.g. or above, if desired; however, hydrocarbon pressures within the range of between 20 p.s.i.g. and 300 p.s.i.g. are found to be most advantageous.

The hydrocarbons suitable for the halogenation reactions described herein include unsaturated aliphatic hydrocarbons such as ethylene, propylene, butylene, butadiene, isoprene, and hydrocarbons containing up to about 10 carbon atoms including isomeric types; and aromatically unsaturated hydrocarbons such as benzene, toluene, xylene and styrene. Of this group, the preferred hydrocarbons are the olefins containing from 2 to 5 carbon atoms and benzene, and most preferably, ethylene. Halogen-substituted hydrocarbons containing at least one hydrogen atom of the above types are also suitably employed in the present invention; of these, vinyl chloride, mono-chlorobutadiene, mono-chloroisoprene, mono- and di-chloroethylene and the corresponding brominated compounds are preferred. Most preferred, however, is vinyl chloride.

The halogenation reactions referred to herein include chlorination, bromination and iodination; although in the case of iodination, olefins are the hydrocarbons halogenated. The most preferred reaction is that of chlorination. Accordingly, the halide catalysts of the present invention are preferably chlorides.

As referred to above, for the purposes of the present invention, the catalyst comprises two distinct components, namely the active catalytic portion as the first component, and the promoting portion as the second component which may or may not be catalytically active, but which aids reaction by the attraction and release of a halogen ion. The active catalytic portion, or first component, is either a cupric halide or a ferric halide, preferably the chloride, and the promoting portion or second component is a dissimilar element halide, preferably where the valence of the element is variable, most preferably at least one chloride selected from the chlorides of bismuth, copper, chromium, cobalt, iron, mercury, molybdenum, nickel, tin, titanium, or vanadium. It is to be understood, however, that at least one halide selected from the halides of silver, gold, zinc, cadmium, boron, aluminium, gallium, indium, thallium, zirconium, hafnium, niobium, tantalum, tungsten or manganese, or mixtures thereof can be suitably employed as the promoter portion of the catalyst. Within this group, most preferred catalyst systems include cupric-cuprous chloride, cupric-ferric chloride, and ferric-chromic chloride. The mol ratio of cupric halide or ferric halide to promoter in the catalyst composition is preferably between 0.01:1 and 100:1, or more preferably between 0.1:1 and 10:1. Halides of ruthenium, rhodium, palladium, osmium, iridium and platinum lower the selectivity of the halogenated product in that they promote the formation of oxygenated compounds. Compounds of these elements are, therefore, excluded.

In the chlorination of an olefinic hydrocarbon, preferably having from 2 to 5 carbon atoms in the presence of an aqueous solution of one of the most preferred catalyst systems, the chlorination temperature is most preferably between 125° C. and 165° C., and the pressure employed is most preferably within the range of 60 p.s.i.g. to 300 p.s.i.g. Generally, the chlorination of saturated hydrocarbons requires a higher temperature with some degree of cracking. Therefore, in these cases, temperatures between 220° C. and 350° C. are employed and for aromatically unsaturated hydrocarbons such as, for example, benzene, a temperature between 180° C. and 300° C. is preferably employed.

The cupric chloride or ferric chloride which is used as the active catalytic portion

of the catalyst to chlorinate a hydrocarbon or a halogenated hydrocarbon the metal of the chloride gives up a chlorine atom, attains a lower valence state and becomes cuprous chloride or ferrous chloride. This spent mixture, when the concentration of the active catalytic portion falls below 90 weight per cent of the original cupric or ferric-chloride content in the solution, is either removed from the reaction zone and regenerated with hydrogen chloride and oxygen, or an oxygen-containing gas, to restore the active cupric or ferric-chloride in a separated regeneration zone or is regenerated within the reaction zone. In the latter case, the chlorination of the hydrocarbon or halogenated hydrocarbon is carried out with the cupric-cuprous chloride catalyst solution simultaneously with the oxygen and hydrogen chloride regeneration of the reduced metal chloride formed. The hydrogen chloride and oxygen in regeneration are used to oxychlorinate the halide of lower valence state, which may be the catalytically active component or the promoter component.

As set forth above, the catalyst is dissolved in water for more intimate contact with reactants in the halogenation zone and as a means of conducting the halogenation reaction at lower temperature, avoiding vaporization of catalyst. In addition to the advantage of being able to conduct the halogenation reactions of the present process at lower temperatures thereby avoiding direct oxidation of the hydrocarbon, the aqueous catalyst solution allows for better overall temperature control in the reactor, which in the case of ethylene chlorination at from 125° C. to 165° C. results in high selectivity to the 1,2-dichloroethane product, a valuable chemical compound and intermediate in the formation of other desirable compounds. The aqueous catalyst systems also result in the conversion to halogenated hydrocarbon at a faster rate than heretofore obtainable.

In the chlorination of ethylene or vinyl chloride in the presence of a most preferred catalyst system, for example, an aqueous cupric-cuprous chloride solution at a temperature not in excess of 185° C., a high selectivity of conversion to 1,2-dichloroethane in the case of ethylene or 1,1,2-trichloroethane in the case of vinyl chloride at least as high as 98 mol per cent based on chlorinated product is obtainable. The 1,2-dichloroethane is a valuable intermediate in the manufacture of vinyl chloride by pyrolysis at 440° C. to 580° C. of the saturated dichloride and the 1,1,2-trichloroethane is an intermediate in the preparation of vinylidene chloride by pyrolysis at a temperature of 380° C. to 600° C. and thus the process using the catalyst of the present invention at a temperature below 165° C.

finds particular commercial value in the economical synthesis of these unsaturated chlorides and provides a new process wherein the hydrogen chloride produced by the pyrolysis of the saturated compounds can be used to at least partially regenerate the catalyst solution. It is to be understood that additional chlorine for regeneration purposes may be supplied as hydrogen chloride or chlorine. The hydrogen chloride concentration is limited to that required for regeneration in order to avoid excess hydrogen chloride being present which would lead to the formation of ethyl chloride in the case of ethylene chlorination.

Another advantage of the present process employing the aqueous catalyst solutions is that an aqueous or dilute solution of hydrogen halide can be fed to the reaction zone in place of the dried, highly concentrated hydrogen halide employed heretofore. In the present process, excess water is vaporized from the reaction zone by the heat of reaction while a portion of that generated serves to maintain the water content of the liquid aqueous catalyst medium. It has also been found that with the catalyst solutions, little or no hydrogen halide is present in the gaseous reactor effluent.

Still another advantage of the present process is that the vapor pressure of the system can be controlled by the addition of certain inert salts such as, for example, sulfates of any of the promoter metals mentioned above, e.g., cupric sulfate, or ferric sulfate. When the vapor pressure of the catalytic solutions is reduced, adiabatic conditions can be achieved at lower pressure at a given per cent conversion per pass or at a given total pressure, a lower conversion per pass is required.

For a better understanding of the present invention, reference is now had to the accompanying drawings, wherein:

Figure 1 shows conditions for a single zone reactor-regenerator;

Figure 2, for a separate reactor and regenerator; and

Figures 3 and 4 illustrate specific embodiments of the process.

Referring to Figure 1, it is found that at a given catalyst solution vapor pressure, e.g. 20 p.s.i.a. and a 10 per cent conversion per pass (plotted on the Y axis), then the total pressure in the reactor which would be required is 47 p.s.i.a. (plotted on the X axis). When the pressure is 30 p.s.i.a., 21 per cent conversion per pass would have been required at the same reactor pressure for adiabatic operation.

In a similar manner, referring to Figure 2, a 10 per cent conversion per pass and a catalyst solution vapor pressure of 20 p.s.i.a., the reactor pressure of 70 p.s.i.a. is required; however, at the same conversion

and a catalyst solution vapor pressure of 50 p.s.i.a., a reactor pressure of 175 p.s.i.a. is required for adiabatic operation.

The apparatus used where the aqueous metal halide catalyst solution is employed, should be composed of, or lined with, acid-resistant materials in order that the catalytic solution will not cause corrosion problems in the system. For example, glass or ceramic-lined equipment is suggested as being both inexpensive and readily available for this type of reaction.

Figure 3 illustrates a process wherein halogenation and catalyst regeneration are carried out in separate zones, namely reactor 3 and regenerator 4. In this operation, air, in place of oxygen can be used as the regeneration gas since the inerts associated therewith (e.g. nitrogen and argon) can be prevented from entering the reactor and causing pressure build up in the system.

According to the process of Figure 3, ethylene is introduced by means of valved feed line 5 and recycle line 6 (hereinafter described) into reactor 3 in contact with an aqueous solution of cupric-cuprous chloride at a rate of 2 gram mols to 200 mols of ethylene per liter of catalyst solution per hour. By way of example, 10.0 gram mols per hour of ethylene is fed per liter of 6 Molar  $\text{CuCl}_2$ —2 Molar  $\text{CuCl}$  catalyst in aqueous solution entering the reactor from line 7 at a temperature of  $170^\circ\text{C}$ . and under 225 p.s.i.g. The vaporous reactor effluent containing chlorinated product and unreacted components (e.g. 1 gram mole per liter per hour of 1,2-dichloroethane; 0.01 gram mol per liter per hour of monochloroethane; 9.0 gram mols per liter per hour of ethylene; and 4.7 gram mols per liter per hour of steam) is withdrawn from reactor 3 by means of line 8 and passed to condenser 10 and then into decanting zone 12 wherein gaseous and liquid phases are separated, at a temperature between  $25^\circ\text{C}$ . and  $80^\circ\text{C}$ . under from 90 p.s.i.g. to 120 p.s.i.g. or approximately the reactor pressure. In the present case, three phases are formed in the decantation zone, namely, a gaseous phase comprising ethylene and monochloroethane; a liquid water phase and a liquid 1,2-dichloroethane phase. The gaseous phase is withdrawn from the decanting zone at a rate of 9.1 gram mols per liter of catalyst per hour in reactor 3, passed through line 14 and line 6 through pump 18 and recycled to reactor 3 as a part of the feed thereto. The aqueous liquid phase is removed by way of line 15 and discarded. The liquid chlorinated hydrocarbon phase is withdrawn from the decantation zone by means of line 20 and passed to cracking zone 22 wherein at a temperature of between  $480^\circ\text{C}$ . and  $580^\circ\text{C}$ ., under from 0 p.s.i.g. to 100 p.s.i.g. (in the present case, at a temperature of

$550^\circ\text{C}$ . under 50 p.s.i.g.), the 1,2-dichloroethane is converted to vinyl chloride in between 25 mol per cent to 85 mol per cent conversion per pass, e.g., 60 mol per cent conversion per pass.

The product mixture from cracking zone 22 is passed to distillation zone 19 by means of line 17. It is to be understood that distillation zone 19 may comprise one or more separate fractionating steps performed in one or several columns. Vaporous hydrogen chloride is withdrawn in line 26 from the distillation zone and recycled to regenerator 4, together with dilute hydrogen chloride feed entering line 26 from valved feed line 28. Unconverted dichloroethane is withdrawn from zone 19 by line 23 and recycled to cracking zone 22, while vinyl chloride product is withdrawn from zone 19 by means of line 29 as the product of the process. The hydrogen chloride separated in distillation zone is withdrawn at a rate of 1 mol per mol of 1,2-dichloroethane reacted. Make-up hydrogen chloride feed and hydrogen chloride from zone 19 is passed to zone 4 with an acid concentration of between 22 weight per cent and 35 weight per cent (e.g. 33 weight per cent acid concentration). Air, at a rate of 2.5 gram mols per liter of catalyst per hour is introduced into regenerator 4 by means of valved line 30 and the oxygen in the air reacts with the dilute hydrogen chloride and cuprous chloride to produce cupric chloride. This regenerates the cuprous-cupric chloride catalyst to its original activity. In operating this process, the mol ratio of cupric chloride to cuprous chloride should not be permitted to fall to the point where cuprous chloride precipitation can cause fouling in the apparatus. The spent catalyst is introduced into regenerator 4 at a rate of 2.3 volumes per volume of catalyst in reactor 3 by means of line 32. The regenerator is operated at a temperature of from  $130^\circ\text{C}$ . to  $150^\circ\text{C}$ . under from 125 p.s.i.g. to 120 p.s.i.g. or at approximately reactor conditions; in the present case, at a temperature of  $150^\circ\text{C}$ . under 125 p.s.i.g. The regenerated cupric-cuprous chloride aqueous solution, the concentration of which is adjusted by the water content of dilute acid from line 28, is then recycled to reactor 3 by means of line 7 through spray heads in the upper part of the tower and inert gases such as, for example, nitrogen, and argon which enter the system in the air feed stream are vented to the atmosphere from the top of the regenerator through valved line 34.

Although the above process utilizes an aqueous cupric-cuprous chloride catalyst to produce 1,2-dichloroethane as an intermediate and vinyl chloride as an end product, it is to be understood that an aqueous cupric-cuprous bromide catalyst, an aqueous

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cupric-ferrous chloride catalyst or a ferric-chromic chloride catalyst or any of the above-mentioned catalyst systems can be substituted in the above description to produce the corresponding 1,2-dihalooethane as an intermediate and, if desired, the corresponding vinyl halide as the end product. In the case of bromide catalyst systems, however, hydrogen bromide in place of the hydrogen chloride is used to regenerate the bromide catalyst systems in regenerator 4. It is also to be understood that vinyl chloride can be substituted for ethylene in the preceding description with any of the above-mentioned catalyst chloride systems to produce 1,1,2-trichloroethane, as an intermediate and vinylidene chloride as the end product.

Figure 4 of the drawings illustrates a process wherein chlorination of a hydrocarbon and catalyst regeneration of the catalyst solution is conducted in the same zone. The following embodiment is described in reference to chlorination; however, it is to be understood that the substitutions discussed above are also applicable in this embodiment of the process.

Ethylene feed entering valved line 35 at a rate of 1.0 gram moles per liter of catalyst solution per hour is passed to line 36 wherein it is admixed with 2.0 gram moles per hour of aqueous hydrogen chloride having an acid concentration of 32 weight per cent and 9.0 gram moles per liter of catalyst per hour of ethylene recycle from line 40 (hereinafter described). This mixture is then passed into reactor 37 wherein, in the presence of 0.5 gram mol of molecular oxygen per liter of catalyst entering zone 37 from valved line 38, the ethylene is reacted with cupric chloride of an aqueous 7 Molar  $\text{CuCl}_2$ —2 Molar  $\text{CuCl}$  catalyst. The temperature in the reaction zone is maintained at  $160^\circ\text{C}$ . and 300 p.s.i.g. is imposed on the mixture in zone 37. By maintaining the above amount of molecular oxygen and hydrogen chloride in this zone, the concentration of cupric chloride is maintained at a steady state and a 10 per cent conversion of ethylene to chlorinated product, of which more than 90 weight per cent is 1,2-dichloroethane, is obtained as a gaseous effluent in admixture with unconverted ethylene.

The gaseous effluent is withdrawn by means of line 42, passed to condenser 44 and the resulting condensate introduced into decantation zone 46 wherein, at a temperature of  $40^\circ\text{C}$ . under 95 p.s.i.g., unconverted ethylene gas is separated in line 48 from liquid 1,2-dichloroethane. Water is withdrawn as a separate liquid phase in line 43 and removed from the process.

The ethylene gas which is withdrawn from zone 46 in line 48 is pressured in pump 50 and recycled to the reaction zone

37 by means of lines 40 and 36 as hereinabove described.

The liquid 1,2-dichloroethane is withdrawn from decantation zone 46 by means of line 52 and passed to cracking zone 54 wherein at a temperature of  $550^\circ\text{C}$ . under 50 p.s.i.g., 1,2-dichloroethane is converted to vinyl chloride and hydrogen chloride in 60 mol per cent per pass. The cracked mixture is then passed by means of line 59 to distillation zone 41 wherein the components of the cracked mixture are separated. Hydrogen chloride is withdrawn as a vapor in line 36 and recycled to reactor 37, together with ethylene feed entering line 36 from valved line 35, and dilute hydrogen chloride feed (20—35 weight per cent) entering line 36 from valved line 60. Unconverted liquid 1,2-dichloroethane is withdrawn from zone 41 and recycled to zone 54 by means of line 58 and the vinyl chloride is recovered from zone 41 as the product of the process by means of line 45. The dilute hydrogen chloride introduced into line 36 serves to maintain required hydrogen chloride feed to the reactor. The concentration of the hydrogen chloride is varied to maintain the water balance in the reactor.

Many modifications of the above-described embodiments illustrated in Figures 3 through 4 will become apparent to those skilled in the art. For example, any of the previously disclosed promoters, particularly  $\text{FeCl}_3$ ,  $\text{CrCl}_3$ ,  $\text{HgCl}_2$ ,  $\text{AlCl}_3$ ,  $\text{TiCl}_4$ ,  $\text{VCl}_3$ , and  $\text{MnCl}_2$ , can be substituted for cuprous chloride in the above catalyst system. It is also to be understood in process using gaseous hydrocarbon that the hydrocarbon or halogenated hydrocarbon may be passed through the aqueous catalyst solution or the aqueous catalyst can be sprayed through the gaseous hydrocarbon phase. The examples which follow are set forth to show the effect of various concentrations in the catalyst system and to provide examples of other hydrocarbons which may be halogenated according to the teachings of this process. However, these examples should not be construed to limit the scope of the present invention.

#### EXAMPLE 1

Into a titanium-lined metal reactor containing 1 liter of an aqueous mixture of 7 M  $\text{CuCl}_2$  and 0.5  $\text{CuCl}$  was added 350 standard cc's per minute of ethylene at a temperature of  $150^\circ\text{C}$ . under a total pressure of 300 p.s.i.g. Under these conditions, 5 mol per cent of ethylene was converted to 1,2-dichloroethane at a selectivity of greater than 98 mol per cent. The remaining portion of the mixture was found to contain ethyl chloride, unreacted ethylene and water.

#### EXAMPLE 2

Two separate glass reactors, the first con-

containing an aqueous solution of 5 M CuCl<sub>2</sub> and 0.5 M CuCl, and the second containing an aqueous solution of 7 M CuCl<sub>2</sub> and 1.0 M CuCl, are both maintained at a temperature of 160° C. Propylene is passed through each of the above solutions at a partial pressure of 100 p.s.i. In the first case, 1,2-dichloropropane is produced in a 1 mol per cent conversion to 1,2-dichloropropane. In the second case, about 2 mol per cent conversion to 1,2-dichloropropane is obtained. This product can be subjected to pyrolysis to yield chloroprenes, if desired.

#### EXAMPLE 3

Into a glass reactor containing 1 liter of an aqueous mixture of 7 M CuCl<sub>2</sub> and 0.5 M CuCl is added 350 standard cc's per minute of ethylene at a temperature of 150° C. The partial pressure of ethylene in the reactor is 120 p.s.i.g. A conversion of 3 mol per cent per pass to 1,2-dichloroethane is obtained. The selectivity of chlorinated product to 1,2-dichloroethane is about 98 per cent.

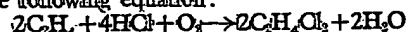
#### EXAMPLE 4

Into a glass-lined autoclave containing 40 ml. of aqueous solution of 7 M CuCl<sub>2</sub> and 0.5 M CuCl is added 0.056 mols of benzene. The temperature in the reaction zone is adjusted to 190° C. and the reaction is allowed to take place over a period of 18 hours, after which the autoclave is cooled to ambient temperature. Upon opening the cooled autoclave, it is found that the benzene layer has disappeared and chlorinated benzenes are produced in about a 10 per cent yield.

#### EXAMPLE 5

To 3 liters of aqueous 7 M CuCl<sub>2</sub>—1 M CuCl catalyst contained in a glass-lined pressure vessel, is passed 4.6 mols of ethylene per hour, at a temperature of about 150° C. and a total pressure of 300 p.s.i.g. Under these conditions, 15 mol per cent of the ethylene is converted per pass to 1,2-dichloroethane with a selectivity for the 1,2-dichloroethane greater than 98 per cent.

The catalyst is maintained in the steady state by the addition of 1.38 mols of hydrogen chloride and 0.345 mols of oxygen per hour. Water is added to replace that which is lost to the system due to carry over with the effluent vaporous mixture containing product which is removed from the reaction zone. The effluent is cooled to condense the 1,2-dichloroethane, while the remaining vaporous unconverted ethylene is recycled to the reaction zone. The reaction taking place in this stage of the process is represented by the following equation:



The condensed dichloroethane is cracked to vinyl chloride and hydrogen chloride at a temperature of 550° C. under 20 p.s.i.g., and

the hydrogen chloride is used in the regeneration spent catalyst. Thus, the overall reaction of the entire process is represented by the following equation:



#### EXAMPLE 6

To a ceramic-lined reactor containing 5 liters of an aqueous catalyst consisting of 1.1 M CuCl<sub>2</sub> and 4.5 M FeCl<sub>3</sub> is added 7.6 mols of ethylene per hour. At a temperature of 150° C. and a total pressure of 300 p.s.i.g. A 25 mol per cent conversion per pass of ethylene to 1,2-dichloroethane is obtained. During the course of an hour, about 30 per cent of the catalyst is removed from the reaction zone per hour and transferred to a separate regenerator wherein 3.8 mols of hydrogen chloride and 9.5 mole of air are admixed with the spent catalyst and the catalyst regenerated.

Since the heat of reaction generated in the reactor and the regenerator is more than sufficient to allow for adiabatic operation, dilute aqueous hydrogen chloride (a 32 per cent solution) is fed to the regenerator along with concentrated hydrogen chloride obtained from a later stage cracking of 1,2-dichloroethane, which cracking is carried out in accordance with Example 5. Under these conditions, water carried into the regenerator is vaporized and carried out of the system together with inerts such as nitrogen and argon which enter the regenerator in the air feed. These vapors are vented to the atmosphere, while the regenerated liquid catalyst is recycled to the reaction zone.

The effluent gas mixture withdrawn from the reactor, containing 1,2-dichloroethane, water, and unreacted ethylene is cooled to condense only the 1,2-dichloroethane and water. The remaining vapor is then recycled to the reactor. The 1,2-dichloroethane is cracked at a temperature of 550° C. under 25 p.s.i.g. to yield vinyl chloride and hydrogen chloride.

#### EXAMPLE 7

Ethylene was passed through 1 liter of an aqueous 1.1 M CuCl<sub>2</sub>—4.5 M FeCl<sub>3</sub> solution contained in a glass reactor at a rate of 1.9 mols per hour. At a temperature of 150° C. under 300 p.s.i.g., 4 mol per cent of the ethylene was converted per pass to 1,2-dichloroethane. The selectivity to the dichloroethane was 95 per cent.

The salts in the above catalyst combination reduce the water vapor pressure of the system to about 45 per cent that of pure water. This reduction in the vapor pressure of water is important in that the system is adiabatic at the reduced pressure and at a lower conversion per pass than that permissible with a higher catalyst vapor pres-

sure. This effect is demonstrated in Figures 1 and 2 referred to above.

#### EXAMPLE 8

5 Into an acid brick lined metal reactor containing 1 liter of 3.75 M CuBr<sub>2</sub>—1.0 M CuBr is passed C<sub>2</sub>H<sub>4</sub> at a rate of 1.6 mols per hour. The total pressure over the system is 300 p.s.i.g. and the temperature 135° C. The conversion to 1,2-dibromoethane is 2  
10 mol per cent per pass with selectivity in excess of 90 per cent.

#### EXAMPLE 9

15 To 3 liters of aqueous 6 M FeCl<sub>3</sub>—1 M MnCl<sub>2</sub> catalyst contained in a glass-lined pressure vessel, is passed 4.6 mols of ethylene per hour. At a temperature of about 160° C. and a total pressure of 300 p.s.i.g. Under these conditions, 15 mol per cent of the ethylene is converted per pass to 1,2-dichloroethane with a selectivity for the 1,2-dichloroethane greater than 90 per cent.

#### EXAMPLE 10

25 Ethylene is passed through 1 liter of an aqueous 6 M FeCl<sub>3</sub>—1 M CrCl<sub>3</sub> solution contained in a glass reactor at a rate of 1.9 mols per hour. At a temperature of 160° C under 300 p.s.i.g., 4 mol per cent of the ethylene is converted per pass to 1,2-dichloroethane. The selectivity to the dichloroethane is about 90 per cent.

30 The salts in the above catalyst combination reduce the water vapor pressure of the system to about 45 per cent that of pure water. This reduction in the vapor pressure of water is important in that the system is adiabatic at the reduced pressure, and at a lower conversion per pass.  
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#### EXAMPLE 11

40 Into a glass reactor containing 1 liter of aqueous 6 M FeBr<sub>3</sub> is passed C<sub>2</sub>H<sub>4</sub> at a rate of 1.6 mols per hour. The total pressure over the system is 300 p.s.i.g. and the temperature 165° C. The conversion to 1,2-dibromoethane is 2 mol per cent per pass with selectivity in excess of 80 per cent.  
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#### EXAMPLE 12

50 To a glass reactor containing 1 liter of aqueous 6 M ferric chloride was passed ethylene gas at a rate of 1.7 mols per hour. At 165° C., and a total pressure of 300 p.s.i.g., the conversion per pass of ethylene was 0.7 mol per cent with a 50 per cent selectivity to 1,2-dichloroethane and a 50 per cent selectivity to ethyl chloride.

#### EXAMPLE 13

55 To a glass reactor containing 1 liter of aqueous 6 M FeCl<sub>3</sub> was passed ethylene gas at a rate of 1.2 mols per hour at 180° C. and at a total pressure of 300 p.s.i.g. The

conversion of ethylene was 2 mol per cent 60 per pass. The product distribution was 95 per cent to ethyl chloride and 5 per cent to 1,2-dichloroethane.

#### EXAMPLE 14

65 To a glass reactor containing 1 liter of aqueous 6 M FeCl<sub>3</sub>—1 M CrCl<sub>3</sub> was passed ethylene gas at a rate of 1.3 mols per hour. At 165° C., under a total pressure of 300 p.s.i.g., the conversion of ethylene was 4.5 mol per cent per pass. The selectivity was 38  
70 per cent with respect to 1,2-dichloroethane and 62 per cent with respect to ethyl chloride.

#### EXAMPLE 15

75 To a glass reactor containing 1 liter of aqueous 6 M FeCl<sub>3</sub>—1 M ZnCl<sub>2</sub> is passed 1.3 mols of ethylene per hour. The temperature is 175° C. and the total pressure is 300 p.s.i.g. The conversion of ethylene is 2 mol per cent per pass and 1,2-dichloroethane is produced in a yield above 50 per cent of the chlorinated product mixture.  
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#### EXAMPLE 16

85 To a glass reactor containing 1 liter of aqueous 4 M FeCl<sub>3</sub>—2 M CrCl<sub>3</sub> is passed 1.3 mols of ethylene per hour. The temperature is 160° C. and the total pressure is 300 p.s.i.g. The conversion of ethylene is 3 mol per cent per pass and 1,2-dichloroethane is more than 50 per cent of the chlorinated product.  
90

#### EXAMPLE 17

95 To a glass reactor containing 1 liter of aqueous 3 M FeCl<sub>3</sub>—3 M ZnCl<sub>2</sub> is passed 1.6 mols of ethylene per hour. The temperature is 160° C. and the total pressure is 300 p.s.i.g. The conversion of ethylene is 3 mol per cent per pass and the selectivity to 1,2-dichloroethane is about 90 per cent.  
100

#### EXAMPLE 18

105 To a glass reactor containing 1 liter of aqueous 6 M FeCl<sub>3</sub> and 1 M AlCl<sub>3</sub> is passed 0.6 mol of propylene per hour. The temperature is 160° C. and the total pressure is 300 p.s.i.g. The conversion of propylene is 1 per cent per pass and the selectivity to 1,2-dichloropropane is 80 per cent.

#### EXAMPLE 19

110 To a glass-lined autoclave containing 1 liter of aqueous 6.6 M FeCl<sub>3</sub> is added 0.5 mol of benzene. The temperature is raised to 190° C. and held there for 16 hours. The conversion of benzene is 50 per cent to mono- and dichlorinated benzene.  
115

#### EXAMPLE 20

To a glass-lined reactor containing aqueous 4 M FeCl<sub>3</sub>—1 M TiCl<sub>4</sub> is passed 1 mol of butadiene per hour. The tempera-

ture is 160° C. and the total pressure is 200 p.s.i.g. The conversion per pass to dichlorinated product is about 1 mol per cent.

#### EXAMPLE 21

5 To a ceramic-lined reactor containing 5 liters of an aqueous catalyst solution consisting of 7 M CuCl<sub>2</sub> and 0.5 M CuCl is added 7.6 mols of vinyl chloride per hour at a temperature of 170° C. and a total pressure of 350 p.s.i.g., a 30 mol per cent conversion per pass of vinyl chloride to 1,1,2-trichloroethane is obtained. During the course of operation, a portion of the catalyst is removed from the reaction zone per hour and transferred to a separate regenerator wherein 4.5 mols of hydrogen chloride and 1.12 mols of oxygen are reacted per hour to regenerate 4.5 mols of cuprous chloride to cupric chloride. The solution so regenerated is recycled to the reactor to maintain the steady state composition.

The effluent gas mixture withdrawn from the reactor, containing 1,1,2-trichloroethane, water, and unreacted vinyl chloride is cooled to condense out the 1,1,2-trichloroethane and water. The remaining vapor is then recycled to the reactor. The 1,1,2-trichloroethane is heated to a temperature of 500° C. under 50 p.s.i.g. to yield vinylidene chloride in admixture with hydrogen chloride. The vinylidene chloride product is recovered by distillation.

#### WHAT WE CLAIM IS:—

1. A process for polyhalogenating an unsubstituted or halogen-substituted hydrocarbon containing at least one hydrogen atom of the olefinic or aromatically unsaturated type which comprises reacting the hydrocarbon with an aqueous composition comprising an aqueous solution of cupric halide or ferric halide and as a promoter at least one halide of a dissimilar element, or a dissimilar valence state of the same element, said element being copper, silver, gold, zinc, cadmium, mercury, boron, aluminum, gallium, indium, thallium, titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, manganese, tungsten, iron, tin, bismuth, cobalt, or nickel, the concentration of the total halides in aqueous solution being between 0.001 mol per cent and 50 mol per cent.

2. A process according to claim 1, in which the hydrocarbon is ethylene, the halides of the catalyst composition are chlorides and the addition product is 1,2-dichloroethane.

3. A process according to claim 2, in which the 1,2-dichloroethane produced is subjected to a temperature of between 440° C. and 580° C. to produce vinyl chloride as the product of the process and hydrogen chloride as a by-product, the activity of the

chloride catalyst mixture being maintained by passing by-product hydrogen chloride through the aqueous catalyst mixture in the presence of oxygen.

4. A process according to claim 3, in which the hydrocarbon is vinyl chloride, the halides of the catalyst composition are chlorides and the hydrocarbon addition product is 1,1,2-trichloroethane.

5. A process according to claim 4, wherein 1,1,2-trichloroethane produced is subjected to a temperature of between 380° C. and 600° C. to produce vinylidene chloride as a product of the process and hydrogen chloride as a by-product, the activity of the chloride catalyst mixture being maintained by passing by-product hydrogen chloride through the aqueous catalyst mixture in the presence of oxygen.

6. A process according to claim 3 or 5, wherein the halogenation of the hydrocarbon and the treatment of catalyst solution with hydrogen chloride in the presence of oxygen are performed simultaneously in the same zone.

7. A process according to claim 3 or 5, wherein the halogenation of the hydrocarbon and the treatment of the aqueous catalyst solution with hydrogen halide in the presence of oxygen are conducted in separate zones.

8. A process according to claim 7, wherein the concentration of the catalyst composition in water is adjusted by dilution of the hydrogen halide feed stream to the catalyst treating zone.

9. A process according to any one of the preceding claims, in which the concentration of the total metal halides in aqueous solution is between 10 mol per cent and 30 mol per cent.

10. A process according to any one of the preceding claims, wherein the mol ratio of cupric halide or ferric halide to promoter in the catalyst composition is between 0.01:1 and 100:1.

11. A process according to claim 10, in which the mol ratio of cupric halide or ferric halide to promoter is between 0.1:1 and 10:1.

12. A process according to any one of claims 1 to 11, in which the catalyst composition comprises cupric-cuprous halide dissolved in water.

13. A process according to claim 12, in which cupric-cuprous halide is cupric-cuprous chloride.

14. A process according to any one of claims 1 to 11, in which the catalyst solution comprises ferric-chromic halide dissolved in water.

15. A process according to any one of claims 1 to 11, in which cupric-ferric halide is dissolved in water.

16. A process according to any one of claims 1 to 11, in which the catalyst com-



position comprises an aqueous solution of cupric chloride and a chloride of  $Cu^+$ , titanium, tin, bismuth, chromium, aluminum, vanadium, zinc, mercury, iron, cobalt, molybdenum or nickel or mixtures thereof.

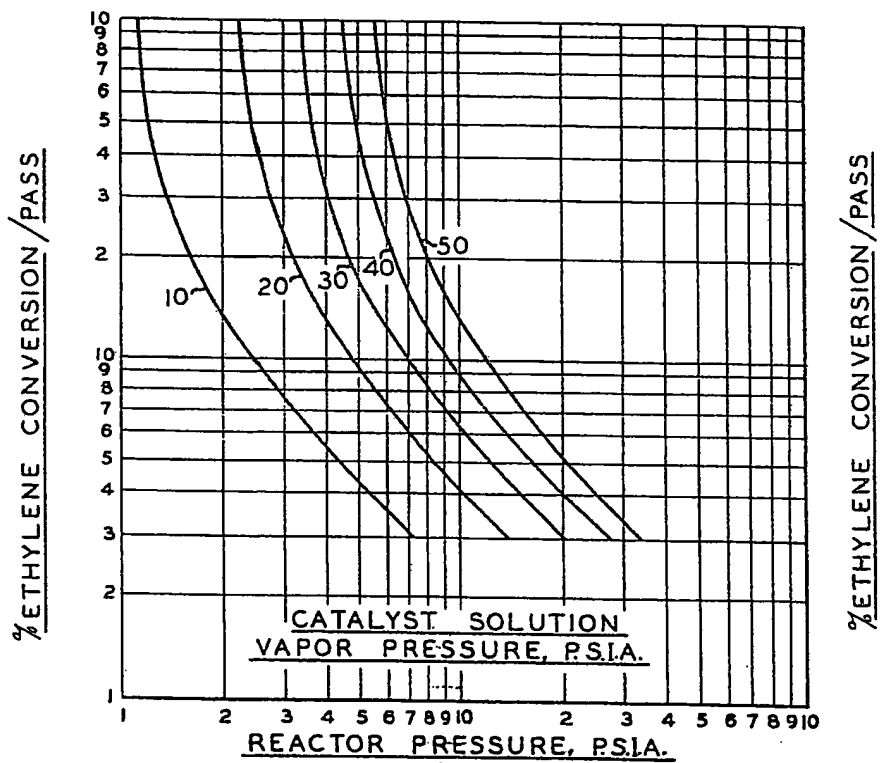
5 17. A process for polyhalogenating an unsubstituted or halogen-substituted hydrocarbon substantially as herein described with reference to the Examples.

18. A halogenated hydrocarbon produced 10 by the process according to any one of the preceding claims.

STEVENS LANGNER, PARRY,  
& ROLLINSON,  
Chartered Patent Agents,  
Agents for the Applicants.

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FIG. 1



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3 SHEETS

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Sheet 1

FIG. 2

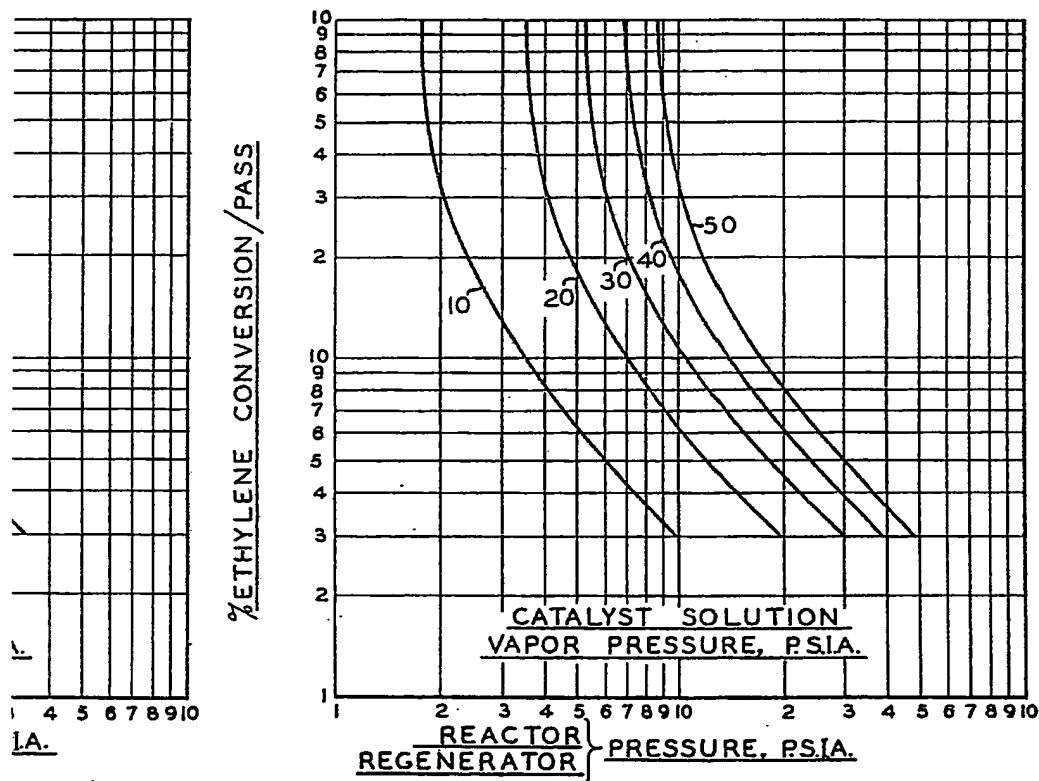


FIG. 1

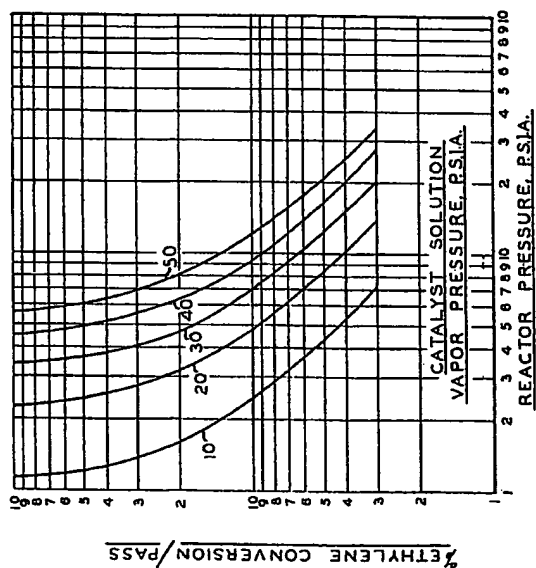
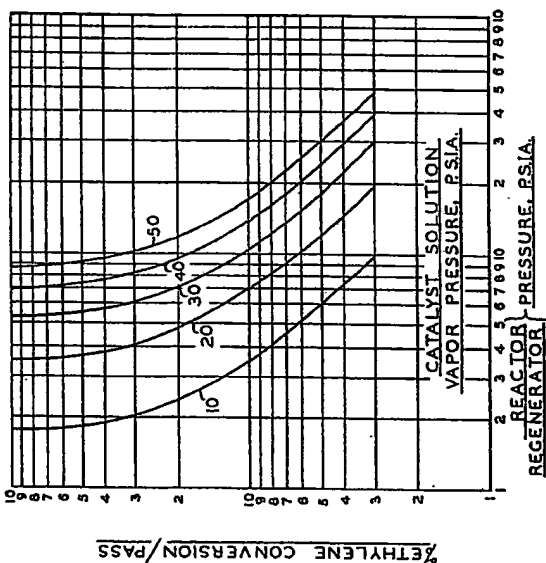
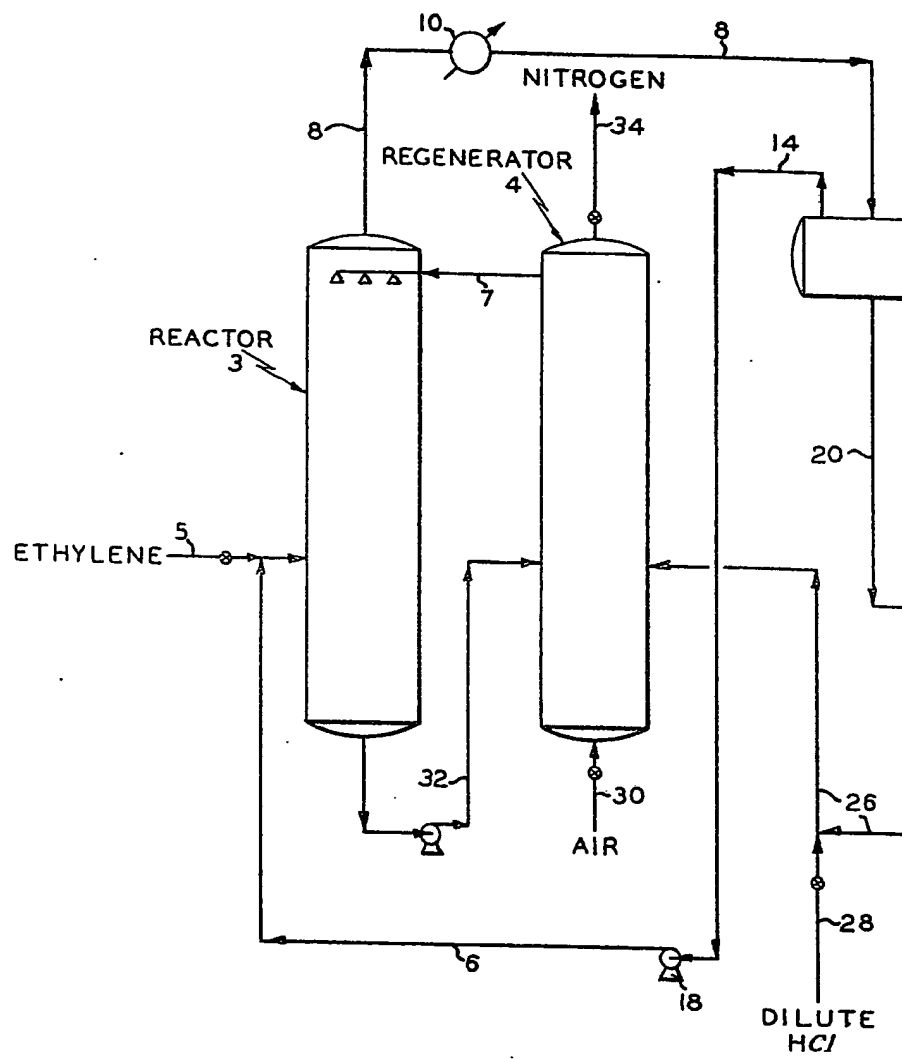


FIG. 2





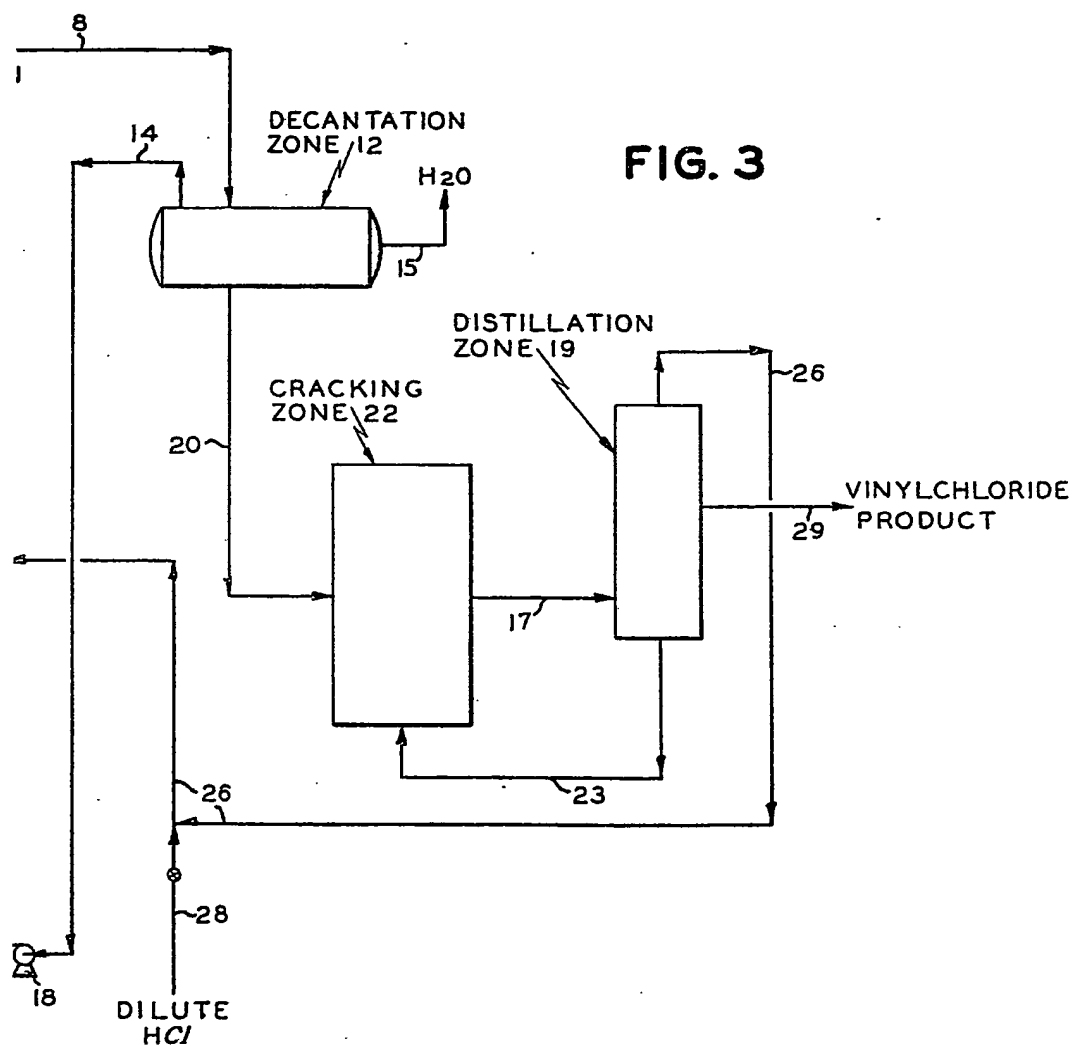
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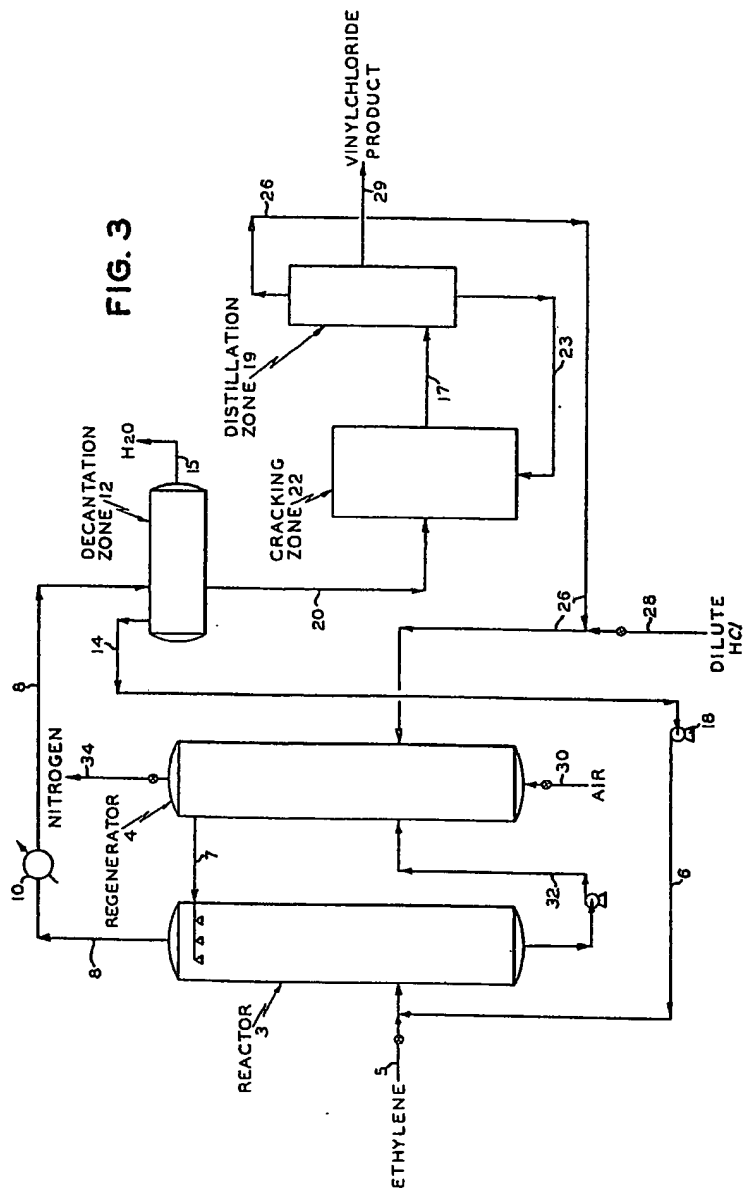
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FIG. 3





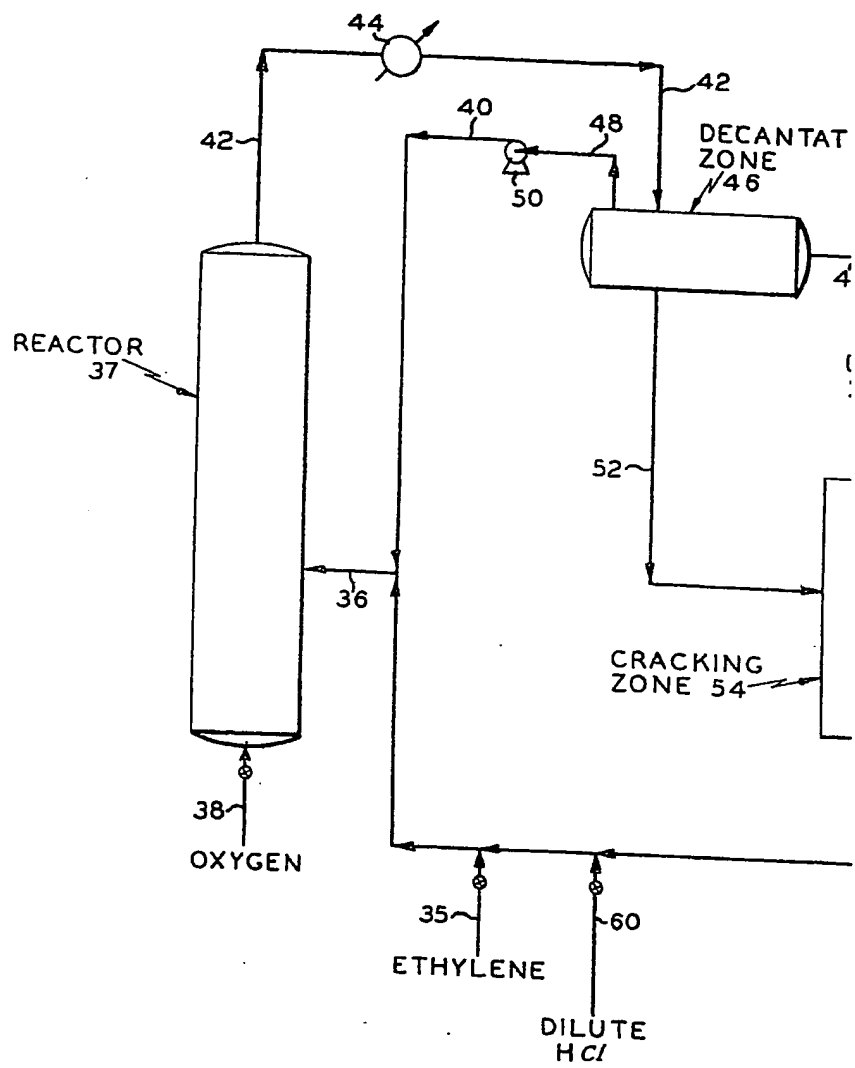




FIG. 4

